OCT 9 1945

REGISTERED NO. M 3121

PROCEEDINGS

OF THE

INDIAN ACADEMY

OF SCIENCES

VOL. XX] *SECTION A* [NO. 4

OCTOBER, 1944

Price Rs. 2 or 3 Sh. *Annual Subscription Rs. 18*

PRINTED AT THE BANGALORE PRESS, BANGALORE CITY, BY G. SRINIVASA RAO, SUPERINTENDENT, AND PUBLISHED BY THE INDIAN ACADEMY OF SCIENCES, BANGALORE.

WAX AND RESIN COMPONENTS OF THE PERICARP OF JAMBUL FRUITS (*EUGENIA JAMBOLANA*)

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Received August 26, 1944

(Communicated by Prof. T. R. Seshadri, F.A.SC.)

In a publication by Rao and Seshadri[1] a preliminary report on the chemical components of the fleshy pericarp of the fruits of *Eugenia jambolana* was made. The note also contains a brief resume of past work on the different parts of the plant. They found that the sweetness of the pericarp was entirely due to the presence of reducing sugars and that there was a total absence of sucrose. The sourness and astringency were attributed to gallic acid and tannin. As partly responsible for the attractive colour the presence of an anthocyanin, Cyanin, was established. But a considerable portion of the colour seemed to be due to the presence of a second pigment which was phenolic in nature and which crystallised from dilute alcohol as snuff-coloured plates melting above 300°. In addition to the colouring matter, two colourless crystalline substances one melting at 149° and another at 232° were also reported to be present. In the present paper the results of a detailed investigation of the wax and resin components of the pericarp are presented.

The dried pericarp was first extracted with methyl alcoholic hydrogen chloride in the cold and on the addition of excess of ether to the extract the colouring matter was completely precipitated. From the alcohol-ether solution was obtained a semi-solid brown residue after complete evaporation and dilution with water. Purification of this using extraction with ether and recrystallisation of ether-soluble matter with alcohol gave an almost colourless solid. Much more of it was obtained by further extraction of the dried pericarp with acetone-ether mixture. The purified solid melted at about 232° with decomposition. This was identical with the substance reported by Rao and Seshadri as melting at this temperature. On close examination it was found to be a mixture, and repeated trials to separate it by crystallisation were unsuccessful. It was then subjected to saponification in the presence of benzene. The unsaponifiable matter contained a sterol and a very small amount of an essential oil and they were separated

by steam distillation. After purification, the sterol melted at 135° and formed an acetyl derivative melting at 120-21°. It seemed to have the same characteristics as the phytosterol obtained by Power and Callan[2] and by Hart and Heyl[3] from the seeds of Jambolana. No detailed identification was possible since the quantity was very small. It was probably a mixture of sterols.

The saponified portion yielded a crystalline potassium salt which was sparingly soluble. The corresponding acid could be easily purified through the potassium salt. It was sparingly soluble in ligroin and could be crystallised from boiling ethyl alcohol. It then melted at 298-300°. Its solution in concentrated sulphuric acid exhibited a strong greenish fluorescence. Though it did not respond to Salkowski reaction it gave a play of colours, pink to green, with the Liebermann-Burchard reagent. It gave no colour with ferric chloride. These properties and the results of analysis indicated that it may be a triterpene acid of the formula $C_{30}H_{48}O_3$ and this was supported by a molecular weight determination by titration (520). It exhibited optical activity, $(\alpha)_D + 78{\cdot}3$ in chloroform solution. It formed a crystalline acetyl derivative but its melting point was indefinite, 150–70°. Its methyl ester was prepared by two methods: (1) heating with methyl iodide and potassium carbonate in anhydrous acetone solution and (2) with diazomethane in anhydrous alcoholic solution. The same substance was produced. Its melting point also was indefinite 161-99°. This was found to be due to hydration, since after drying at 110° for 2 hours the melting point went up and it melted at 195-99°. The ester could further be acetylated and the acetate of the methyl ester melted at 214-16°. Thus it was clear that the original compound was a hydroxy acid of the triterpene series. Tests with fish indicated that it was toxic.

A comparison with known compounds showed close similarity with oleanolic acid. Oleanolic acid was obtained from several sources and has been examined by various workers who gave it a number of names. Power and Tutin[4] first isolated 'oleanol' from the leaves of olive tree and characterised it as a dihydric alcohol having the molecular formula $C_{31}H_{48}O(OH)_2$. From *Eugenia caryphyllata* (cloves), caryophyllin[5] was isolated in a pure form and its properties were compared with urson, a compound which was isolated from the skins of grapes and which was nearly identical with caryophyllin. Van der Haar[6] showed that the two substances oleanol and caryophyllin were identical, in spite of the slight variations in the recorded properties of the various derivatives and that they were not dihydroxy compounds but monohydroxy monocarboxylic acids. In view of this he assigned the name 'oleanolic acid' to the substance. The following table furnishes the

comparison between the properties of the substance isolated from Jambul fruits and those of oleanolic acid :—

	Colourless substance from Jambul fruits	Oleanolic acid
Molecular formula	$C_{30}H_{48}O_3$	$C_{30}H_{48}O_3$
M.P. of the substance	298–300°	306–308°
Specific rotation	$[a]_D$ +78·3°	$[a]_D$ +79·5°
Methyl ester (m.p.)	195–199°	196–198°
Acetyl derivative of methyl ester (m.p.) ..	214–216°	223°
Toxicity to fish	Toxic	Toxic

Experimental

About 2 Kg. of the dried pericarp of the fruits of *Eugenia jambolana* were extracted with 4 litres of methyl alcoholic hydrogen chloride (2.5%) at room temperature for a period of 2 weeks. The extract was filtered and treated with 10 litres of ether to precipitate the colouring matter, which was separately examined. The ether-alcohol mixture free from the colouring matter was distilled to recover the solvents. The last traces of alcohol were removed in an open basin and then diluted with water (600 c.c.). The entire product, pasty and resinous in nature, was extracted repeatedly with small amounts of ether and the combined ether extracts concentrated. The light greenish brown residue was then taken up in alcohol and recrystallised. The resulting substance was almost colourless and began to melt at 232° (decomp.).

The pericarp residue left behind after methyl alcoholic hydrogen chloride extraction was refluxed twice with 3 litres of acetone-ether mixture (1 : 1) and the combined extracts distilled off to recover the solvents. The substance obtained was taken in hot alcohol and recrystallised. The resulting product was found to be identical with the above and therefore they were combined (yield 5 g.) and treated further.

The substance was saponified for 12 hours with alcoholic potash (8%) in the presence of benzene so as to effect complete saponification. The alcohol was then distilled off and the soap taken in a large excess of water and repeatedly extracted with ether. The filtered ether extracts on evaporation left behind a semi-solid unsaponifiable matter (A). The aqueous caustic potash solution contained a large amount of colourless solid. It was filtered and the residue of potassium salt was collected (B). The alkaline solution on acidification and boiling gave rise to a solid (C) which was filtered.

Unsaponifiable matter (*A*) (*Sterol and essential oil*).—It had a sweet smell which indicated the presence of an essential oil. Further it gave the Salkowski reaction as well as the play of colours with Liebermann-Burchard reagent. This gave a clue that it might contain a sterol. Therefore, with a view to separate the essential oil, it was subjected to steam distillation. The essential oil obtained had a refractive index, 1·464. Nothing more could be done since it was very small in quantity.

The residue in the flask left after steam distillation was repeatedly extracted with ether and the combined extracts concentrated. The product thus obtained was twice recrystallised from alcohol and a shining crystalline substance melting at 135° was obtained (yield 0·5 g.). It gave all the sterol reactions and its acetate melted at 121°.

Potassium salt (*B*) (*isolation of a triterpene acid*).—The crystalline potassium salt was treated with dilute hydrochloric acid, boiled and filtered. The solid acid thus obtained (3 g.) was then heated with 40 c.c. of $\frac{1}{2}$N alcoholic potash and 15 c.c. of water for an hour and a half, the solution filtered while hot and then allowed to cool slowly, when only a very small amount of the porduct separated. Therefore, most of the alcohol was removed and the salt allowed to crystallise. The crystalline salt (rectangular rods) was dissolved in 3 parts of cold methyl alcohol, filtered and the salt precipitated from the alcoholic solution by the addition of water. The salt thus obtained was taken in 10 parts of methyl alcohol and to it was added a slight excess of strong HCl in order to liberate the free acid.

The resulting acid was filtered and repeatedly boiled with solvent petrol so as to remove any petrol-soluble portions and then recrystallised from ethyl alcohol thrice. The crystalline substance (rectangular prisms) obtained melted at 298–300°. It was soluble in hot alcohol, acetone, ether, chloroform and benzene. It gave a strong greenish fluorescence with conc. H_2SO_4. It did not give the Salkowski reaction but gave a play of colours, from pink to green with Liebermann-Burchard reagent. It contained no methoxyl group [Found: C, 73·4; H, 11·0; loss on drying, 7·2%. $C_{30}H_{48}O_3$ $2H_2O$ requires C, 73·1; H, 10·6; H_2O (loss) 7·3%.] Its minimum molecular weight (*i.e.*, equivalent weight) as determined by titration with alkali was 520. It had a specific rotation in chloroform solution of $(\alpha)_D$ + 78·3°.

Derivatives.—The acetate of the above acid was obtained by boiling with acetic anhydride in presence of sodium acetate. When recrystallised from aqueous alcohol, it was found to melt indefinitely between 150° and 170°. Even after reacetylation the melting point did not improve. The combus-

tion analysis, however, agreed with the monoacetate of the acid. (Found: C, 76·6; H, 10·5; $C_{32}H_{50}O_4$ requires C, 77·1; H, 10·1%.)

The *methyl ester* of the acid was prepared by heating with excess of methyliodide and anhydrous potassium carbonate in dry acetone medium for 30 hours After distilling off the solvent the residue was treated with water in order to remove inorganic salts. The product was then purified by first extracting with ether in which it was soluble. It was finally recrystallised from aqueous acetone (1 : 1) or aqueous alcohol. It was obtained in the form of needles with indefinite melting point, 163-99°. The ester nature of this product was established by titration with alkali. (Found: OCH_3, 6·1; $C_{31}H_{50}O_3$ requires OCH_3, 6·6%.)

The methyl ester was also prepared in a different way. The acid was dissolved in anhydrous methyl alcohol and treated with excess of diazomethane in ethereal solution. The product when recrystallised was found to be indentical with the sample described above. Suspecting that the presence of water of crystallisation was the cause of indefinite melting point, the ester was dried at 110–15° for 2 hours. It was then found to melt at 195–99°. The melting point of the methyl ester of oleanolic acid found in the literature is 196–98°.

The acetyl derivative of the above methyl ester was prepared by boiling with acetic anhydride and anhydrous sodium acetate. It was first recrystallised from ethylacetate using a little decolourising carbon and finally from ethylacetate-alcohol mixture. It appeared as colourless needles and had a melting of 214–16°. (Found: C. 76·8; H, 10·4; no loss on drying; OCH_3, 6·5; $C_{33}H_{52}O_4$ requires C, 77·3, H, 10·2; OCH_3, 6·1%.)

Solid (C).—This on treatment with solvent petrol could be separated into two fractions: (*i*) easily soluble and (*ii*) sparingly soluble. The former was waxy in nature indicating it to be a fatty acid mixture. The latter on recrystallisation from methyl alcohol gave a substance melting at 240° and exhibiting all the properties of the acid obtained from (B). The yield of the fatty acid mixture was, however, very small for a detailed examination.

Toxicity.—35 mg. of the acid (*B*) was dissolved in 5 c.c. of rectified spirit and the solution added to 1000 c.c. of water contained in a wide trough. Fish were introduced into the water and they showed symptoms of toxicity within 2 hours thus indicating the toxic action of the substance to fish.

Summary

The waxy matter of the pericarp of *Eugenia jambolana* was saponified using alcoholic potash. The unsaponifiable matter contained a little

sterol and some essential oil. A sparingly soluble potassium salt was produced which yielded a triterpene hydroxy acid. A study of its properties and of its derivatives indicates that it is oleanolic acid. It seems to be the major component of the waxy matter.

The authors wish to express their gratitude to Prof. T. R. Seshadri for his guidance and interest throughout the investigation.

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CONDENSATION OF MALONANILIC ACID WITH ALDEHYDES

Part VII. Condensation with 6-Nitro-piperonal, 6-Bromopiperonal, 5-Bromovanillin and 5-Bromoveratraldehyde: Influence of several dissimilar Groups

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Received April 4, 1944

The influence of single groups like the hydroxy, methoxy, nitro, methyl and the haloid present on the ring of the aromatic aldehyde, when the aldehyde is condensed with malonic acid and with malonanilic acid, with or without pyridine, has been sufficiently obvious in the work described in the earlier papers of the two series. The general observation has been that the hydroxy, particularly in the orthoposition to the aldehyde group, is the most deterrent, the hydroxy in other positions is less so, the methyl in the para is still less, the methoxy and the nitro are only very slightly so, while the chloro and the bromo are distinctly favourable to quicker reaction and larger yields.

In the last paper, Part VI[1], condensations were described where the aldehyde had serveral groups that were either alike or different, and as in the aldehyde-malonic acid condensation, so, with of course differences of degree, in the aldenyde-malonanilic acid condensation, the groups that are alike have reinforced the influence of the single group, while dissimilar groups have modified the influence of one another. In the present paper the study of these condensations with malonelic acid has been extended to still more complicated aldehydes, that is to aromatic aldehydes having even a larger number of groups, *e.g.*, to 6-nitro-piperonal and 6-bromopiperonal, and to 5-bromovanillin and 5-bromoveratraldehyde. It must be stated that here the situation is no longer as simple or as clear as before and that the generalisation holds but without uniformity; the features are already too complex to permit the results to be easily predictable or understandable.

We may take piperonal for instance, Piperonal-malonic acid condensations, conducted in the presence of a trace (=0·15 or about 1/6 mol.) of pyridine, have been among the most successful of the series (Vahidy and Pandya, 1935[2]): these are understandable as the two hydroxy groups are

far away from the aldehyde and are completely replaced by methylenedioxy group. With malonanilic acid, the condensation gave two different products, one in the absence and the other in the presence of pyridine-trace, *viz.*, 70·7% of the piperonylidene-malonanilic acid and 90% of the 3:4-methylenedioxycinnamanilide respectively (Ittyerah and Pandya[1]). The 6-nitro- and the 6-bromo-piperonal give results where the maximum yields are still comparable. 6-Nitropiperonal gives, in the absence of pyridine, 78·9% yield, made up of 30·9% acid and 48% cinnamanilide, while, with the pyridine-trace, it gives 76·9% of the cinnamanilide alone. The maximum is thus distinctly below the 90%, again showing that the nitro group is not so very favourable in the pyridine-trace condensation as it is in the Perkin's condensations.[3] It may also be noted that the maximum yield with the pyridine-trace needed eight hours' heating on waterbath: with decreased heating (*e.g.*, five hours) the yield was less, *viz.*, 74·6%, composed of 16·9% acid and 57·7% cinnamanilide. A stronger base like piperidine in traces induced resinification (which happened so much in the condensation of dinitrobenzaldehyde[4]), from which only 16% (3·2% acid and 12·8% cinnamanilide) could be isolated.

The influence of the bromine group is clear in 6-bromopiperonal, where bromine occupies the same position that the nitro group did. The more powerful effect is seen in the maximum yield of 90·9% of the cinnamanilide obtained with a trace of piperidine: the pyridine trace gave a little less yield than the nitroderivative, however, namely, 63%, made up of 40% acid and 25% cannanamilide. With glacial acetic acid, there was no decarboxylation, but the yield was 78.3% of the aicd. A strange part here was that in the absence of any of the condensing reagents mentioned above, no product was obtained, much of the aldehyde being recovered unchanged or sublimed.

The efficiency of bromine-group was expected to show itself very decisively in the bromine derivatives of vanillin and veratraldehyde, which both were prepared from vanillin. As protocatechuicaldehyde gave little condensation-product with malonanilic acid[1], vanillin with one hydroxy group methylated gave 19·% acid and 59·5% cinnamanilide, respectively in the absence and presence of pyridine[1], and varataldehyde with no hydroxy group gave 36·7% acid and 91·8% anilide respectively,[1] higher yields still were looked forward to from their bromo-derivatives. But 5-bromovanillin and 5-bromoveratraldehyde did not sustain this expectation.

5-Bromovanillin gave no reaction when there was no condensing reagent: and gave no acid product, whatever condensing agent was used. With

piperidine-trace it gave 28·7%, with glacial acetic acid (Haydruck's method[5]) also 28·7%, with pyridine-trace 57·5%, with pyridine-piperidine at room temperature (three weeks, Vorsatz' method[6]) also 55·7% of the cinnamanilide, while when heated with the pyridine-piperidine mixture it only gave tar. The bromo-derivative here gave less than vanillin while the expected acid did not make its appearance at all.

5-Bromoveratraldehyde has however done almost the reverse: it gave a slightly higher yield of the acid in the absence of any condensing agent, *viz.*, 49·2%, compared with 36·7% from the unbrominated aldehyde, but with pyridine or piperidine it simply went into resin from which nothing useful could be isolated.

Possibly 6-bromovanillin and 6-bromoveratraldehyde might show better results: at least they could compare batter with 6-bromopiperonal.

The products described above and in the Experimental are all new. Identical or very similar conditions of condensations have been tried. Greater modifications are being tried in order to avoid resin-formation if possible.

Of these four aldehydes, only two 6-nitro-piperonal and 6-bromopiperonal have so far been condensed with malonic acid, when they gave 93 and 81% yields respectively (unpublished, Miss R. Pandya), in the presence of a trace of pyridine.

Experimental

Condensation with 6-Nitropiperonal

6-Nitropiperonal was prepared by the method described by Pandya and Verghese.[7] The usual procedure of the experiments was similar to what has been described earlier, with occasional differences that have been metnioned.

With no Condensing Agent.—The 6-nitropiperonal and malonanilic acid were heated together (1 : 1 mol.) on a water-bath for five hours. The acid and the anilide both were obtained here in yields of 30·9 and 48% respectively. The 6 ni-tro 3 : 4-methylenedioxy-cinnamanilide came out in pale yellow needles melting at 198°. Found N = 8·92%, the cinnamanilide $C_{16}H_{12}O_5N_2$ requires 8·97%. It was recrystallised from acetone and alcohol. The acid recrystallised from alcohol came out in long pale yellow needle crystals, melting at 238°. Found N = 8·24%, 6-nitro-3 : 4-methylenedioxy-benzylidenemalonanilic acid $C_{17}H_{12}O_7N_2$ requires 7·86%. It also gave a bright yellow silver salt which gave. (Found Ag = 24·06%, the

salt $C_{17}H_{11}O_7N_2Ag$ requires 23·3%.) Ray and co-workers[8] describe the acid but give 230° (dec.) as the melting point of it, which must be less pure.

With a Trace of Pyridine.—With the usual trace of pyridine and five hours' heating on water-bath, the same two products, but now in a different ratio, came out: the acid was less 16·9%, and the anilide 57·7%, making the total yield 74·6%. Heating on the waterbath for eight hours changed the whole product into the cinnamanilide, which was a little higher 76·9%. Higher temperature, such as 110–115° induced resinification and reduced the yield.

With Piperidine trace.—The mixture became dark even at the ordinary temperature, while heating gave much tar and little product (about 5% acid and 13% anilide).

Condensation with 6-Bramopiperonal

The 6-bromo-piperonal was prepared from piperonal by the method of Parijs.[9] It melted at 129°; yield = 45%.

Without a Condensing Agent.—There was no reaction, even when the temperature was raised to 120°.

With Glacial Acetic Acid[5].—1·2 g. 6-bromopiperonal, 0·9 g. malonanilic acid and 1 c.c. glacial acctie acid were heated together on a water-bath. The sodium carbonate gave a sodium salt that was insoluble even when digested with hydrochloric or sulphuric acid. Ammonium carbonate was therefore used which gave a 78·3% yield of the 6-bromo-piperonylidene-malonanilic acid, melting at 226° (dec.). Though the acid came out from alcohol in pale yellow needles, it turned deep yellow just before melting. (Found: N = 3·56%, the acid $C_{17}H_{12}O_5NBr$ requires 3·59%. Found Br = 20·91, 20·33%, the aicd requires 20·51%.)

With a Trace of Piperidine.—Heated on waterbath for five hours and extracted with alcohol, gave the 6-bromo-3: 4-methylenedioxycinnamanilide, melting after recrystallisations from alcohol at 191°. (Found N = 4·18%, $C_{16}H_{12}O_3NBr$ requires 4·05%. Found Br = 23·32%, the anilide requires 23·12%. Yield = 90·9%.)

With a Trace of Pyridine.—It gave total yield of 65% made up of 40% acid and 25% anilide.

Condensation with 5-Bromovanillin.—

The 5-bromovanillin was prepared from vanillin by the method of Dakin[10]: m.p. 164°, yield 90%.

Without any Condensing Reagent.—No reaction happened at 100°. At 125° the whole mass became liquid, after which the temperature was gradually lowered. There was no reaction however.

With Pyridine.—Five hours on waterbath gave no acid, but only the 5-bromo-4-hydroxy-3-methoxy-cinnamanilide in shining colourless crystals melting at 200–201°. Yield 57·5%. (Found N = 4..11%, the cinna manilide $C_{16}H_{14}O_2NBr$ requires 4·02%.) It dissolved in soda or potash solutions giving yellow solutions. It dissoved in concentrated sulphuric acid also giving a yellow colour, which on heating changed first to green then to dark.

With a Trace of Piperidine.—Much tarry matter from which about 28·7% of the cinnamnitide was recovered.

With Pyridine-Piperidine Mixture.—The product was tarry, even after four hours' heating Vorsatz's method[6] gave 57·5 of the cinnamanilide. 0·6 g. 5-bromovanillin, 0·9 g. malonanilic acid, 1·4 g. pyridine and 2 drops piperidine were mixed and kept at room temperature (20–25°) for three weeks, when a solid cake was obtained. This was treated with ammonium carbonate solution but it had no action. The residue was the cinnamanilide (yield = 57·5%).

With Glacial Acetic Acid[5].—Eight hours on waterbath, when the mass became yellow and green. Only 28·7% of the anilide was obtained.

Condensation with 5-Bromoveratraldehyde.

This aldehyde was prepared from bromovanillin by ordinary methylation by means of dimethyl sulphate and potassium hydroxide. It came out in 82·6 yield, melting at 62°.

Without any Condensing Agent.—2·5 g. 5-bromoveratraldehyde and 1·8 g. malonanilic acid were heated in a flask on waterbath for five hours. After fusion and effervescence, the colour changed from straw yellow to pale green. Sodium carbonate solution dissolved it, leaving some unacted aldehyde. The alkali extract lost its colour when washed with ether. The sticky mass set on cooling and when recrystallised from alcohol, came out as colourless crystals melting at 198° (dec.). Yield = 49·2%. (Found N = 3·56%, the 5-bromoveratrylidenemalionanclic acid $C_{18}H_{16}O_5NBr$ requires 3·44%.) With longer time at lower temperature, twelve hours at 90° only 39·3% of the acid was isolated.

With a Trace of Pyridine.—Five hours on waterbath or with a higher temperature, a nonacid viscous mass was obtained from which nothing could be separated. So also with a pyridine-piperidine mixture on three hours' heating nothing could be separated.

Summary

Malonanilic acid have been condensed under different conditions, with 6-nitro-piperonal, 6-bromopiperonal, 5-bormovanillin and 5-bromoveratraldehyde. The reactions with the first two give yields that may be more or less expected. The last two give some unexpected features, particularly 5-bromoveratraldehyde from which the expected cinnamanilide has not yet been isolated or obtained. All the products described in the paper are new.

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EXPERIMENTS IN THE GROUP OF SYMPATHOMIMETICS

Part V. Relation between Chemical Constitution and Pressor Activity of Possible Sympathomimetics derived from the Benzene, Naphthalene, Phenanthrene and Isoquinoline Rings

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Received August 26, 1944

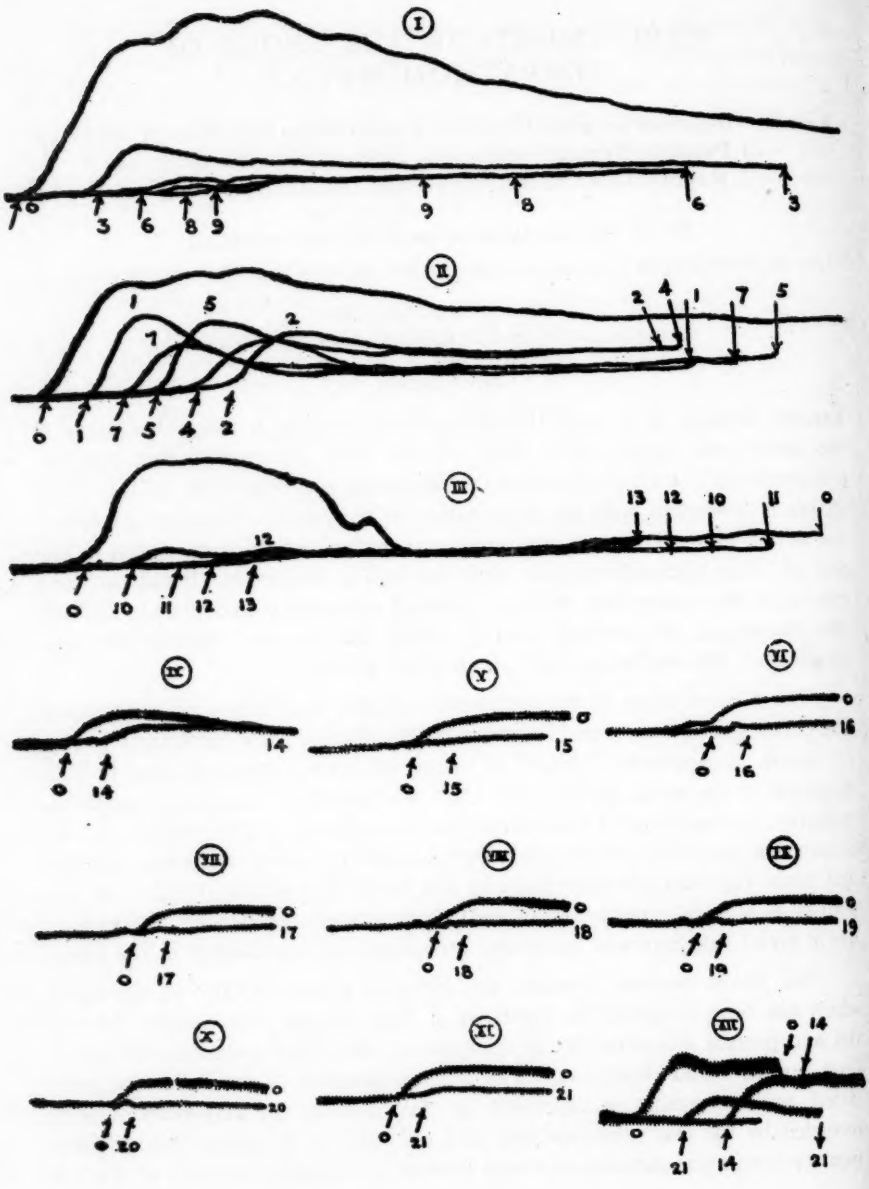
(Communicated by Prof. T. R. Seshadri, M.A., Ph.D., F.A.SC.)

Introduction

EARLIER sections dealt with the syntheses of a series of bases, belonging to the carbo- and hetero-cyclic ring systems and possessing the requisite configurations for sympathomimecity (Rajagopalan, 1940, 1941, 1944). This section is concerned with the presentation of the results of subjecting twenty-one of the above group of compounds to preliminary biological tests in respect of their sympathomimetic activities and a discussion, based on these results, of the relationship between chemical constitution and pressor activity. The compounds are derived severally from the benzene, naphthalene, acenaphthene, phenanthrene and isoquinoline nuclei.

The pressor effect in the spinal cat was used as a means of comparison. The collection of twenty-one compounds was divided into convenient groups or single compounds. Each of these was then compared directly with tyramine in the same animal. Of the two available standard sympathomimetics, tyramine rather than adrenaline was chosen as the control for the reason that the results obtainable with tyramine are known to be less variable and more reproducible than those of the latter base (Gurd, 1937). All the amines as well as tyramine were used as their water-soluble hydrochlorides. Their serial numbers and molecular structures are represented in the table.

The blood pressure tracings are given in graphs I–XII. In the table, which has been compiled on the basis of these graphs, the pressor intensities and pressor durations of the compounds have been given in addition to their numbers and structures. The pressor intensity of the substance compared with tyramine is expressed as the ratio of the maximum pressure recorded by the test substance and that recorded by tyramine. Pressor duration represents the *duration at a high level of the individual activity* of the test


I
II
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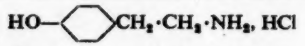
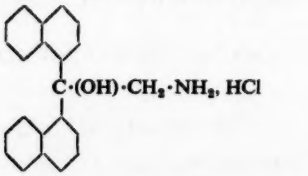
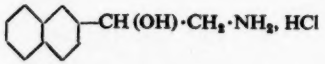
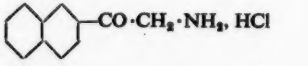
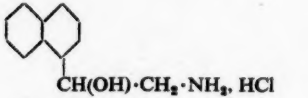
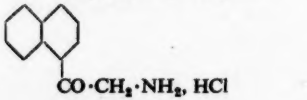
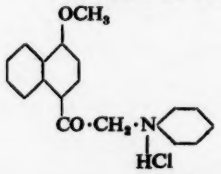
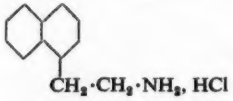
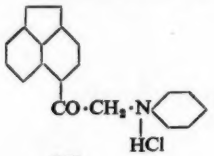
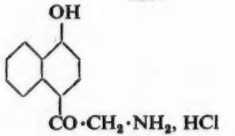
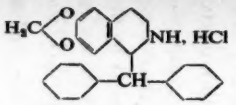
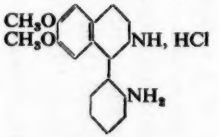
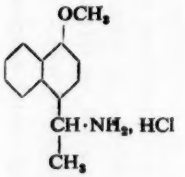
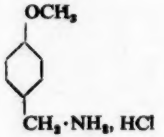
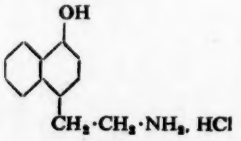
IV
V
VI
VII
VIII
IX
X
XI
XII

Serial No.	Name (hydrochloride of)	Structure	Pressor Intensity (Tyramine =1)	Pressor Duration (Tyramine =+++)
0	Tyramine		1	+++
1	β, β-1 : 1'-Dinaphthyl-β-hydroxy ethylamine		9/13	+
2	β, 2-Naphthyl-β-hydroxy ethylamine ..		11/26	++++
3	ω-Amino-β-acetonaphthone		1/40	+
4	β, 1-Naphthyl-β-hydroxy ethylamine ..		5/13	++++
5	ω-Amino-α-acetonaphthone		15/25	+
6	4-Methoxy-ω-piperidino acetonaphthone ..		3/40	+

Serial No.	Name (hydrochloride of)	Structure	Pressor Intensity (Tyramine =1)	Pressor Duration (Tyramine =+++)
7	β, 1-Naphthyl ethylamine		5/13	+
8	ω-Piperidino-5-acetoacenaphthone ..		3/40	±
9	4-Hydroxy-ω-aminoacetonaphthone ..		1/20	+
10	β, β-9 : 9'-Diphenanthryl-β-hydroxy ethylamine	$(9\text{-}C_{14}H_9)_2 : C(OH)\cdot CH_2\cdot NH_2$, HCl	4/23	++
11	Dibenzyl aminomethane	$C_6H_5\cdot CH_2\cdot CH(NH_2)\cdot CH_2\cdot C_6H_5$, HCl	3/23	++
12	β, β-Diphenyl-β-hydroxy ethylamine ..	$(C_6H_5)_2\cdot C(OH)\cdot CH_2\cdot NH_2$, HCl	2/23	++
13	β, β-*Bis*-(4, hydroxy naphthyl-) ethylamine	$(4\text{-}HO\cdot C_{10}H_6)_2CH\cdot CH_2\cdot NH_2$, HCl	2/23	++
14	N, N'-Trimethylene *bis*-tyramine ..	$(HO\cdot C_6H_4\cdot CH_2\cdot CH_2\cdot NH\cdot CH_2)_2 : CH_2$, 2 HCl	5/7	++++
15	β, β-Diphenyl ethylamine	$(C_6H_5)_2 : CH\cdot CH_2\cdot NH_2$, HCl	trace	trace
16	β, β-Diphenyl-β-hydroxy-α-benzyl ethylamine	$(C_6H_5)_2 : C(OH)\cdot CH(NH_2)\cdot CH_2\cdot C_6H_5$, HCl	trace	trace
17	1-Diphenylmethyl-1 : 2 : 3 : 4-tetrahydro-6 : 7-methylenedioxy isoquinoline		trace	trace

17	1-Diphenylmethyl-1 : 2 : 3 : 4-tetrahydro-6 : 7-methylenedioxy isoquinoline		trace	trace
18	1-(*o*, Amino-) phenyl, 1 : 2 : 3 : 4-tetrahydro-6 : 7-dimethoxy isoquinoline		trace	trace
19	*a*-(4-Methoxy naphthyl-) ethylamine ..		trace	trace
20	4-Methoxy naphthyl methylamine ..		trace	trace
21	4-Hydroxy napthyl ethylamnie ..		3/7	+

A2

compound. On the basis that the pressor duration of tyramine is represented by + + +, the signs have been assigned under this column against each compound. It should be borne in mind that the reasons for assigning the signs are subjective and unlike pressor intensity, these cannot be construed to have any quantitative significance.

It has been possible, in the present study to examine only one aspect of the sympathomimetic effects, namely, that on blood pressure. That the relative values obtained by different workers differ somewhat widely and that the animals used, the mode of anæsthesia employed, the less obvious differences of technique, as well as individual variations of response in animals of the same species, all affect the results have already been pointed out by Barger and Dale (1910). Further, that the blood pressure depends on these and on the resultant of a number of other independent factors—rate and force of heart beat, tone of the visceral blood vessels, tone of the blood vessels in the skeletal muscles (which later in turn depends on the balance between the vasoconstrictors and vasodilators) and the state of the capillary bed, any or all of which may be affected by an injection of a sympathomimetic amine—and that the determination of the relative efficiencies of sympathomimetics by this method has only a conventional value until the results are analysed in the light of observed actions on other organs innervated by the sympathetic nerves have been emphasised by Barger and Dale (1910) and a few others (Rosenbleuth, 1932; Rosenbleuth and Cannon, 1933; Gurd, 1937).

In view of the reasons, however, which originally stimulated the studies on possible sympathomimetics belonging to the various ring systems, the attempt has been made to ascertain how far the present biological data furnish information under the following heads:

(*i*) the fundamental relationship, if any, existing between structure and pressor action of compounds belonging to the naphthalene series;

(*ii*) the possibilities held out by the observation of Madinaveitia (1919, 1920) that the mere substitution of the naphthalene ring in place of the customary benzene nucleus of pressor amines results in an augmentation of pressor activity by over 40 times;

(*iii*) the intrinsic sympathomimetic merits of poly- and hetero-cyclic rings when present in compounds possessing the requisite structure for pressor action;

(*iv*) the possibilities held out by the observation of von Braun *et. al.* (1916, 1917) that methyl amino hydrindene owes its intense activity to its being doubly a β-phenyl ethylamine; and

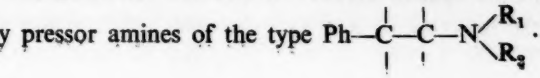
(*v*) the course of the future search for sympathomimetics.

Experimental

The experimental technique adopted was as follows: The cat was anæthetised with chloroform-ether and secured on its back. A trecheal cannula was then inserted and both carotids were tied at their distal ends. The animal was turned over and the second vertebra was exposed by a crucial incision on the mid-line so as to get at the foramen magnum. A probe was inserted through the foramen up into the cranium and the brain was completely destroyed by gentle manipulation. The cranium was plugged with cotton-wool smeared with vaseline to stop bleeding, if any, completely. Soon after, the spinal cord was destroyed and similarly plugged with cotton-wool. The administration of ether-chloroform was discontinued at this stage and artificial respiration was instituted immediately before the cord was cut. The cut edges of the skin were then sutured and the cat was turned over on its back. The blood pressure was recorded in the usual way by inserting a cannula in the left carotid artery and attaching to it a mercury manometer provided with a plunger carrying a writing point which was adjusted to write on the smoked paper of a slowly moving kymograph. Another cannula was inserted into the left femoral vein which was tied at its distal part; this cannula was connected by a small rubber tubing to a burette containing normal saline solution. The administration of the drugs was effected by injecting their solutions into the rubber tubing followed by running in a definite volume of the saline solution in order to ensure the complete influx of the full dose into the circulation. The dosage consisted of 1 c.c. of a one-in-thousand solution of each of the drugs and corresponds to 1 mg. of each of the base hydrochlorides. The doses were injected into the animal in succession, the period between two doses being not much longer than that required for the blood pressure to return to its initial level.

Discussion

The *a*-naphthyl methyl amines (Nos. 19 and 20) (Dey and Rajagopalan, 1939) possess extremely feeble activities. The results would go to show that these bases, pharmacologically and chemically, bear great resemblance to the feebly active benzylamines rather than to the active β-phenyl ethylamines.

The ω-amino methyl ketones of the naphthalene series studied are Nos. 3, 5, 6, 8 and 9. Of these, 4-methoxy, ω-piperidino acetonaphthone (No. 6) and ω-piperidino acetoacenaphthone (No. 8) were only feebly active, the activity being 3/40 of that of tyramine. This is of course consistent with the low activities shown by pressor amines of the type  .

However, the other members of the group (Nos. 3, 5 and 9) are of particular interest. Comparing Nos. 3 and 5, which are isomeric and also exhibit considerable activities, the influence of the manner of substitution of the side-chain in the naphthalene ring becomes apparent: substitution at the α-position (No. 5) is more than twice as effective as that in the β-position (No. 3) of the naphthalene nucleus. It then becomes of interest to enquire into the effect of introduction of a hydroxyl group in the nucleus *para* to the side-chain of the most active member of this group, namely, ω-amino-α-acetonaphthone (No. 5). An answer is provided by a comparison of Nos. 5 and 9. Such introduction of a nuclear hydroxyl group (No. 9) reduces not only the intensity (nearly 12 times) but also the duration of pressor action of the original compound (No. 5). This result is surprising and hardly in keeping with what could have been expected from knowledge of the benzenoid pressor amines; it is also in conflict with the previous findings of Madinaveitia who, as a result of testing the same pair of compounds on the isolated frog heart by the Trendellenburg technique, observed the hydroxylated base (No. 9) to be considerably more active than the related nuclear-unsubstituted compound (No. 5).

As under the group of β-naphthyl ethanolamines and β-naphthyl ethylamines, the four available compounds (Nos. 2, 4, 7 and 21) have been tested. The isomeric β-naphthyl ethanolamines (Nos. 2 and 4) are of equal effectiveness in respect of both intensity and duration of pressor action. The alcoholic bodies differ from their precursors, *viz.*, the ω-amino methyl ketones (Nos. 3 and 5) in an interesting manner: whereas substitution of the side-chain at the α-position was twice as advantageous as that in the β-position of the aromatic ring as far as the amino ketones (Nos. 3 and 5) were concerned, this effect of position substitution is destroyed on reduction to the corresponding carbinols (Nos. 2 and 4).

Further comparison of the carbinols (Nos. 2 and 4) with their parent ketones (Nos. 3 and 5) serves to bring out other characteristics of the alcoholic function. In the first place the transition from the ketone to the alcohol in one case (No. 3 to No. 2) is accompanied by an intensification of pressor action, while a similar transformation in another (No. 5 to No. 4) results in a lowering of the original activity. In the second place, the passage from the ketones to the alcohols in both cases produces greater duration at a higher level of pressor action. The latter characteristic as well as the intensification of activity noted in one set (Nos. 3 and 2) is conceivable in the light of experience with sympathomimetics of the benzene series, but the lowering of activity in another (Nos. 5 and 4) is quite unexpected.

Still further significance of the alcoholic group in the naphthalenic sympathomimetics is brought to light by a scrutiny of the activities evinced by three compounds of the present series, *viz.*, the isomeric β-naphthyl ethanolamines (Nos. 2 and 4), and β-1-naphthyl ethylamine (No. 7). As might have been anticipated all the three possess equal intensity of action and the first two, having an alcoholic hydroxyl group in their side-chains, to take on the characteristic of more pronounced duration at a higher level of pressor action.

The activities exhibited by ω-amino-α-acetonaphthone (No. 5) on the one hand, and on the other by β-, *l*-naphthyl ethyl amine (No. 7) are of interest. Although there is no difference in their duration of action, the ketone (No. 5) is more active (ca. 1½ times) than the ethyl amine (No. 7) and is the reverse of what obtains in analogous benzene types.

Comparison of the activities of β, 1-naphthyl ethylamine (No. 7) and its nuclear substituted derivative, β, 4-(hydroxy naphthyl-) ethylamine (No. 21) serves to ascertain further the implications of introducing nuclear (or phenolic) hydroxyl groups. Analogy with benzeneoid sympathomimetics suggests a high enhancement of activity but a diminution of the duration of action. Actually, however, introduction of a hydroxyl group in the *para*-position in β, 1-naphthyl ethylamine (No. 7) confers on the resulting product (No. 21) only a trace of enhancement of the original intensity without however, influencing the duration of action.

In connection with the inquiry about the extent to which the present results lend support to Madinaveitia's generalisation that the mere substitution of the naphthalene ring in place of the benzene nucleus of customary pressors gives rise to an enhancement of activity by over 40 times, it becomes necessary to study pairs of strictly comparable compounds belonging to the benzene and naphthalene series. In the present series only two such pairs, namely β, β-diphenyl, β-hydroxy ethylamine (No. 12) and its corresponding naphthyl analogue (No. 1), and tyramine and its analogue 4-hydroxy naphthyl ethylamine (No. 21), have been available. Comparisons between β, 1-naphthyl ethylamine (No. 7) and β-phenyl ethyl amine and between the isomeric ω-aminoacetonaphthones (Nos. 3 and 5) and ω-amino acetophenone have also been made from a knowledge of the data formerly presented by other workers on β-phenyl ethylamine and ω-aminoacetophenone, respectively (Barger and Dale, 1910; Barger, 1930; Hartung, 1931). They reveal firstly that the quantitative relationship between pressor amines severally derived from benzene and naphthalene are somewhat obscure, and secondly, that in some instances (Nos. 1, 3, 5 and 7) there results considerable increase of activity, while in one case (No. 21) there is decreased

activity, as a consequence of substitution of the naphthalene ring in place of the benzene nucleus. To an extent, the activities of Nos. 1 and 5 and to a lesser extent that of No. 3 may be construed to lend support, to the generalisation of Madinaveitia, who, it will be recalled, based his finding on the result obtained by comparing only a single pair of analogous compounds.

Comparison of three analogous compounds (Nos. 12, 1 and 10) affords some measure of the merits of benzene, naphthalene and phenanthrene ring structures when present in sympathomimetics. It appears that the phenanthrene ring is nearly twice as effective and the naphthalene ring about seven to eight times as effective as the benzene ring. Again comparing Nos. 6 and 8, there does not seem to be any difference sympathomimetically between the naphthalene or acenaphthene nuclei of pressor amines.

Next, in the order for examination, comes up the question of how far the expectations regarding the sympathomimetic potentialities of compounds, whose synthesis was specifically actuated by the explanation of the mode of intense action of methyl amino hydrindene by von Braun, have now been realised. Among members of the series of bases derived severally from the various ring systems and whose molecules contain the repeating active atom-patterns. Ar. C. C. N - (Nos. 1, 10–18), only two, namely, Nos. 1 and 14, possess considerable activities; the others possess feeble (Nos. 10–13) or only a trace (Nos. 15–18) of sympathomimetic activity. If, as visualised by von Braun, methyl amino hydrindene owed its high activity to its being doubly a β-phenyl ethylamine, a high degree of activity should have been recorded at least for Nos. 11, 12, 14, 15, 16 and 17, since each of these can be construed as β-phenyl ethylamines in more ways than one. The low activities shown by these, however, make it clear that the mode of activity of methyl amino hydrindene, although at present beyond comprehension, should be conceived to be different from that envisaged by von Braun. The observed activities of the present series of compounds constitute yet another illustration, so plentiful in chemotherapy, of the fact that the effect produced by substituting groups in a physiologically active molecule is not necessarily additive or cumulative, but that their effects may be reciprocally modifying.

Finally, there remains for consideration the course of the future search for sympathomimetics. It is seen that except in the naphthalene series, new potent pressors are probably unlikely to be encountered in any of the other ring systems, namely, the benzene, acenaphthene, phenanthrene and isoquinoline rings. Besides bringing out the inadequacy of von Braun's concept of the mode of activity of methyl amino hydrindene, the results now

obtained serve to prove definitely that further study of compounds possessing the repeating, active moieties, Ar. C. C. N– in their structures may not lead to sympathomimetics of surprisingly high or useful pressor potencies.

While the above results no doubt give some insight particularly into the fundamental relation between chemical constitution and pressor action of naphthalenic sympathomimetics, it becomes obvious that the rules governing similar relationship among the benzenoid compounds apply to the corresponding members of the naphthalene series only to a limited extent. The present investigations also bring out the essential differences in the physiological activity of compounds derived from the two ring systems. These and evidence of the existence of inexplicable chemotherapeutical contrasts such as that provided by the observed but essentially unpredictable effects produced by the hydroxyl group when present either in the nucleus or the side-chain of naphthalenic pressors preclude attempts to formulate the relationship between chemical constitution and sympathomimetic action of compounds derived from ring systems other than benzene. The reason, therefore, for advancing the tentative conclusions concerning the naphthalene series is that the evidence now available indicates such trends. That there should be some legitimate doubt about some of these is necessarily implied in any attempt to compare and correlate the none too abundant data in a realm where there are as many variables as there are in biological experimentation. A more definite formulation may, however, be expected to be possible after the accumulation of very much more pertinent information by extended investigations.

Summary

Twenty-one selected compounds derived severally from benzene, naphthalene, acenaphthene, phenanthrene and isoquinoline have been examined for their pressor activities in the spinal cat, using tyramine as the control.

The α-naphthyl methylamines resemble benzylamine in exhibiting feeble activities. Fair degrees of activity are shown by the ω-amino acetonaphthones, the β-naphthyl ethanolamines and the β-naphthyl ethylamines. The rules governing the qualitative and quantitative relation between structure and pressor action of benzenoid sympathomimetics seem to apply to members of the naphthalene series only to a limited extent. The substitution of the benzene nucleus of pressor bases by the naphthalene ring generally results in considerable increased activity, but this has an exception. Consequently, the generalisation of Madinaveitia that such substitution augments the activity by over forty times receives only limited support. The

postulate of von Braun that methyl amino hydrindene owed its intense activity to its being doubly a β-phenyl ethylamine appears inadequate in view of the low activity evinced by a number of bases which may be considered as β-phenyl ethylamines many times over. While the naphthalene and acenaphthene nuclei are equal and about seven times as effective as the benzene ring the phenanthrene ring is only twice as effective. New potent pressors appear unlikely to be encountered in the benzene, phenanthrene and isoquinoline ring systems, but the naphthalene series seems to be promising.

Acknowledgements

Our thanks are due to Messrs. A. N. Ratnagiriswaran, M. R. Subramania Sastri, R. Ramaswami and K. Velayudhan Nair for help during the course of this investigation and to Professors P. C. Guha, B. B. Dey and T. S. Tirumurti for their kind interest. We are in addition, thankful to the Government of Madras for the award of a Research Scholarship to one of us (S. R.)

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THE THEORY OF THE THERMAL EXPANSION OF DIAMOND

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Received September 1, 1944

(Communicated by Sir C. V. Raman, Kt., F.R.S., N.L.)

1. *Introduction*

In two papers appearing in these *Proceedings* (Dayal, 1944 *b*, *c*), the author has successfully evaluated the thermal expansion of the alkali halides from the known law of force between the constituent ions, and on the basis of the Raman dynamics of crystal lattices. In the case of diamond, the same procedure cannot be followed because of the co-valent nature of the bindings. On the other hand, the thermal expansion of diamond is interesting from several standpoints. In the first place, a direct experimental test of the validity of the Grüneisen theory of the thermal expansion has been made by Dr. Nayar (1941) by measuring the variation with temperature of the principal Raman line of diamond. In the second place, the thermal expansion data are available over a wide range of temperature. The results of the measurements, below the room temperature, have been quoted by Grüneisen (1926), while the region between the room temperature and 1000° K. has recently been investigated by Dr. R. S. Krishnan in this Institute (under publication). Dr. Saxena (1944), has shown that Nayar's spectroscopic observations cannot be explained on the basis of the usual form of the Grüneisen theory, but that they find an easy explanation if the frequencies could be divided into two groups with different Grüneisen constants. In the present paper, the author has evaluated the Grüneisen constants of the eight frequencies of the diamond lattice given by the Raman dynamics, and has thus been able to explain Nayar's results and the observed thermal expansion data satisfactorily.

2. *The Evaluation of the Grüneisen Constants*

In the paper on the specific heat of diamond (Dayal, 1944 *a*), the lattice frequencies were calculated with the help of the three force constants, *viz.*, K, K″ and K_α. The first two of these arise from the mutual displacements of the neighbours and the next nearest neighbours respectively, while the third is involved in the changes of the various valence angles. We have to determine how these force constants change with the alteration of the

crystal volume. The volume dependence of K, and K″ can be investigated by following the Grüneisen method (*l.c.*). He assumed that the potential energy between the two atoms separated by a distance r, is of the form $-\frac{a}{r^m}+\frac{b}{r^n}$, where a, b, m and n are constants. m was kept equal to three in all cases, but n was varied to give a correct value of the thermal expansion. We use the following modification of the Grüneisen equation for the potential energy between the neighbouring atoms, which is suggested by the well-known Morse function

$$\phi = D\left[\frac{r_e^{2m}}{r^{2m}} - \frac{2r_e^m}{r^m}\right] \tag{1}$$

ϕ is the potential energy between the atoms separated by a distance r, r_e is their equilibrium distance, D is the dissociation energy per bond and m is a constant. This function has all the usual properties of the Morse function. For $r = r_e$, it gives the dissociation energy D. It also satisfies the equilibrium condition. If we put $\frac{m}{r_e}$ equal to a, which is the constant of the Morse function, the two functions give the same second derivative, *i.e.*, the same force constant. We will use the same law of force (with the same m) for an atom and its next nearest neighbours, as has been done by Grüneisen. In order to preserve the equilibrium condition we have, however, to replace r_e by kr_e, where k is the ratio of the distance between the next nearest neighbours to that between the neighbours and is equal to $\frac{2\sqrt{2}}{\sqrt{3}}$. For m, we use the value 3·1 which is practically identical with the value (3) used by Grüneisen. We will show later that the use of this constant gives a reasonable value for the heat of vaporisation of diamond. It can be easily seen that

$$\frac{\partial K}{\partial r_e} = -\frac{3K(m+1)}{r_e} \text{ and } \frac{\partial K''}{\partial r_e} = -\frac{3K''(m+1)}{r_e}. \tag{2}$$

The volume dependence of K_α, cannot be investigated so easily, but we expect that it will be much less than that of K and K″. We make the assumption that K_α depends so little on the volume that we can put $\frac{\partial K_\alpha}{\partial r_e} = 0$. The Grüneisen constants of the various frequencies can now be obtained easily by differentiating the frequency expressions given in the earlier paper (*a*). The values, so calculated, have been given in Table I. The numerical values of the frequencies and Bhagavantam's group theoretical symbols (1943) have been given in the same table for the convenience of reference. In the case of the elastic spectrum, the value given by Grüneisen (1·1) has been assumed to be correct.

TABLE I

Grüneisen Constants for the Vibration Frequencies of Diamond

ν cm.$^{-1}$	1332	1149	784	1248	1088	1013	1284	565	Elastic ν_{es} (573)
Group theoretical designation	F_2	H_1	H_2	H_4	K_3	K_1	M_1	M_2	..
γ	1·37	1·51	0·82	2·0	2·0	1·14	1·34	0·82	1·1

Saxena had used a Grüneisen constant 0·834 for the frequencies H_2 and M_2, which is almost identical with the value calculated here. For all the other frequencies, he employed a common value 1·403 which explained Nayar's spectroscopic observations as well as the observed thermal expansion. Our value of the Grüneisen constant for the frequency 1332 cm.$^{-1}$, used by Nayar is 1·37 and the average of the Grüneisen constants for the remaining frequencies is not very different from the value used by Saxena. The present calculations, therefore, provide a theoretical justification for his results.

3. Evaluation of the Thermal Expansion Coefficients

According to the theory discussed in the paper on the thermal expansion of the alkali halides (Dayal, *b*) the coefficient of cubical expansion α of diamond is given by

$$\alpha = \frac{K_0}{V_0} \frac{\frac{3R}{48}\left[\sum_1^8 \gamma_j \sigma_j \, E\left(\frac{h\nu_j}{kT}\right) + 3\gamma_D \, D\left(\frac{\theta_D}{T}\right)\right]}{\left[1 - \frac{3m+1}{6} \cdot \frac{K_0}{V_0} \Sigma \gamma_j \sigma_j E_j\right]^2} \qquad (3)$$

where K_0 and V_0 are the compressibility and the atomic volume at the absolute zero of temperature and pressure. γ_j is the Grüneisen constant of a frequency ν_j and σ_j is the number of degrees of freedom corresponding to the same. E and D are the Einstein and the Debye functions of specific heat and E_j is the thermal energy content of the frequency ν_j. The frequencies and their degrees of freedom are given in an earlier paper (*a*). The co-efficients of the thermal expansion calculated from the equation (8) are given in Table II. The mean experimental values have been taken from Grüneisen's article (*l.c.*), where full references are given. The true coefficients above 300° K. are taken from the smoothed curve of Dr. R. S. Krishnan (under publication). The change of the frequency ($\Delta\nu$) with the temperature for the 1332 line of diamond has also been calculated and given

in the same table along with Nayar's experimental values. The formula used for this purpose is (Saxena, *l.c.*)

$$\Delta \nu = \gamma_{1332}\, \bar{\alpha}\, (T_2 - T_1)\, \nu,$$

where $\bar{\alpha}$ is the mean thermal expansion coefficient between the temperatures T_2 and T_1. Adams' value of compressibility $\cdot 16 \times 10^{-12}$ cm.^{2}/dyne (1921) has been used in calculation and the quantity $\frac{3m+1}{6}$, etc., in the denominator has been neglected, being very small for a crystal of small thermal expansion like diamond. The atomic volume has been taken as 3·42. It will be seen that the agreement between the calculated and the observed thermal expansion is quite good. There is a small discrepancy in the range 400 to 500° K., but this is the region where the experimental errors are likely to be large. The change in the frequency observed by Nayar (*l.c.*) agrees with the calculated value above 400° K. At lower temperatures the calculated values are much lower. It is possible that the difference may be due to the errors of measurement which must be very large due to the difficulty of correctly measuring the fraction of a wave number.

TABLE II

The coefficients of thermal expansion and the temperature variation of 1332 *Raman line of diamond*

Temperature ° K	$\alpha \times 10^6$ (Calculated)	$\alpha \times 10^6$ (Experimental)	$\Delta\nu$ (cm.$^{-1}$) (Calculated)	$\Delta\nu$ (cm.$^{-1}$) (Experimental)
84 –194	·47	·54*		
194 –273·2	1·81	1·74		
273·2–296·2	2·82	2·91		
194 –296·2	2·04		·37	·8
300	3·26	3·25†	·80	1·2
400	5·5	6·0	1·20	1·35
500	7·7	8·15	1·57	1·60
600	9·5	9·55	1·82	1·85
700	10·4	10·55	1·99	2·0
800	11·4	11·4	2·16	2·2
900	12·1	12·2	2·27	2·4
1000	12·7	..	3·07	3·3
1130	13·1	..		

* From Grüneisen (*l.c.*). † From Krishnan (under publication).

4. *Heat of Vaporisation of Diamond*

In the earlier paper (*l.c.*), K and K″ were evaluated as $3{\cdot}14 \times 10^5$ and $0{\cdot}39 \times 10^5$ dynes/cm. respectively. On using these values in the function (1) we can obtain the dissociation energies of the bonds between the neighbours and those between the next nearest neighbours. Since there are 2 N bonds joining the atoms to their neighbours and 6 N joining them to their next nearest neighbours, the total energy of dissociation per gm. atom at the absolute zero can be calculated as 226 K. cals. This compares well with the latent heat of diamond quoted by Slater (1939) as 199 K. cals. The heat of dissociation of a single $C-C$ bond comes out as 57 K. cals, which is slightly lower than the value found in the organic compounds. This is, perhaps, due to the presence of the forces between an atom and its next nearest neighbours.

In conclusion, the author wishes to record his grateful thanks to Professor Sir C. V. Raman, KT., F.R.S., N.L., for his interest in the work. He is also thankful to Dr. R. S. Krishnan for showing him his unpublished results of the thermal expansion of diamond.

Summary

A modification of the Grüneisen formula for the force between the atoms, suggested by the Morse function, has been used to evaluate the Grüneisen constants of the eight vibration frequencies of diamond given by the Raman dynamics of crystal lattices. It has been assumed that the force constant K_a of the angular distortion does not change, with the change of the crystal volume. The thermal expansion of diamond is then calculated and shown to be in good agreement with the measurements at low temperatures, quoted by Grüneisen and with the experimental data at high temperatures, of Dr. R. S. Krishnan. Nayar's spectroscopic observations on the change of the Raman line of diamond with temperature have been quantitatively explained. The heat of vaporisation of diamond has been computed and shown to be in reasonable agreement with the value estimated from other considerations.

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THE THERMAL EXPANSION OF METALS AT LOW TEMPERATURES

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Received September 1, 1944

(Communicated by Sir C. V. Raman, Kt., F.R.S., N.L.)

1. Introduction

In two papers appearing in these *Proceepings* (Dayal, 1944 *b,c*), the author calculated the Grüneisen constants of the vibration frequencies of the alkali halides, and drew attention to the incorrectness of the Grüneisen assumption that this constant is the same for all the frequencies of the spectrum. It was shown there, that the ratio of the coefficient of thermal expansion to the specific heat is not a constant, but decreases continuously with the fall of temperature. In the present paper, the author has examined the latest data for the thermal expansion and the specific heat of the five face-centred metals, *viz.*, Al, Cu, Ag, Au and Pb, of the three body-centred metals namely, W, Li and Na, and of one diamond-like metal silicon, to find out if there are any systematic deviations from the Grüneisen law. The specific heats of these metals were previously studied by the author on the basis of the Raman theory of the crystal vibrations (Dayal, 1944 *a*). Potassium had to be eliminated from the present study, because its thermal expansion data are not available.

2. Face-Centered Metals

According to Grüneisen (1926), the thermal coefficient of cubical expansion α is given by the following formula

$$\alpha = \frac{C_v}{Q_0\left[1 - k\frac{E}{Q_0}\right]} \tag{1}$$

C_v is the specific heat per gm. mol at constant volume. Q_0 is a constant given by $\frac{V_0}{\gamma K_0}$, where V_0 is the molecular volume and K_0 the compressibility, both at the absolute zero of temperature and pressure. γ is the Grüneisen constant $-\frac{\partial \log \nu}{\partial \log V}$. E is the thermal energy given by integral $\int_0^T C_v\, dT$, and k is a constant related to the exponents of the attractive and

the repulsive forces in the atoms. According to the Grüneisen theory, k lies between 2 and 3. The small correction term $k\frac{E}{Q_0}$ in the denominator is important only at the higher temperatures, and generally, brings about a change of about 10%. near the room temperature. The Grüneisen constant γ, appearing in Q_0 and the constant k, are both semi-empirical constants. It is, therefore, usual to select them empirically in comparing the Grüneisen theory with the experimental data. C_v is, likewise, determined from an empirically determined Debye function, which is afterwards compared with the characteristic temperature obtained from the experimental specific heat data. It is apparent, from the method of selecting the constants, that the small deviations from the Grüneisen theory cannot be detected, and only striking discrepancies will come to notice.

Aluminium.—Nix and MacNair (1941, called henceforwards *a*, and 1942, called *b*), have recently made what they have themselves described as extremely accurate determinations of the thermal expansion of various metals of extreme purity, between the range 90 to 800° K. Two systems of fringes, one giving the thermal expansion, and the other the change in the temperature through the change in the dielectric constant of fused silica, are photographed simultaneously on a 16 mm. standard movie film at frequent intervals. A quasi-continuous record of the change in the length and the temperature was thus obtained at one and the same time. They found that the thermal expansion of aluminium can be accurately predicted by the equation (1), over the whole range of temperature (90–800)° K., if C_v are obtained from a characteristic temperature 400, and k and Q_0 are assumed to be 2·7 and 83·6 K. cals. respectively (*a*). The characteristic temperature, in this range of temperature, as obtained from the latest specific heat measurements of Giaque and others (1941) is 389° K. If we use the actual values of C_v, as given by the above workers, and keep the other constants unchanged, there is a small deviation of about 3% in the calculated and the experimental values of α at 90° K. At higher temperatures the difference is less.

The data of Nix and MacNair are in fairly good agreement with the earlier measurements (between 87 and 315° K) of Buffington and Latimer (1926). There is a small difference of about 3% between their measurements and those of Ebert (1928) in the liquid-air region. The latter's measurements, however, extend to 48° K. The constants used by him are $\theta = 381$, $k = 2{\cdot}7$ and $Q_0 = 86{\cdot}1$ K. cals., which do not differ very much from Nix and MacNair's constants. There is a very good agreement between the calculated and the experimental data of Ebert throughout, except at 48° K.,

where the difference between the two is about 20%. A deviation of about 12% is also noticeable in the experimental and the calculated mean coefficients between -190 and $-253°$ C. The specific heats used by him do not differ from the experimental values of Giaque (*l.c.*) by more than 2–3% at any point covered by his measurements.

Copper.—The thermal expansion of this metal has been the subject of a large number of investigations. Simon and Bergmann (1930), measured it at the various temperatures in the range -180 to 0° C., and found that their data did not fit in with the Grüneisen theory, which gave a value of α about half the experimental value at 95° K. Their results have, however, not been confirmed by any other worker, so that they must be ascribed to some unknown source of error.

Nix and MacNair fitted their data (*a*) in the range ($-185{\cdot}5$ to 500)° C. by the equation (1), by taking $\theta = 325$, $k = 2{\cdot}8$ and $Q_0 = 120$ K. cals. The specific heat values, used by them, have a maximum difference of about 4% from the experimental values (Giaque, *l.c.*). Their experimental values of α are, according to them, in quite good agreement with the earlier measurements of Adenstedt (1936), of Buffington and Latimer (*l.c.*), and of Dorsey (1907). The last two have not compared their results with the Grüneisen theory. Adenstedt has used the same values of the constants k and Q_0 as Nix and MacNair, but his value for θ is 315, which is in better agreement with the specific heat data. Measurements of the thermal expansion have also been made by Keesom, Agt, and Miss Jansen (1926), and by Borelius and Johnasson (1924). As shown by the former, their data agree amongst themselves and with those of Dorsey (*l.c.*) within 2%. They are, therefore, in quite good agreement with Nix and MacNair's results. The experimental data of Keesom and collaborators extend to 20° K, and thus afford a test of the Grüneisen theory at very low temperatures. The values of the mean coefficients obtained by them in the ranges -100 to $-180°$ C. and -180 to $-250°$ C. are $12{\cdot}35 \times 10^{-6}$ and $5{\cdot}45 \times 10^{-6}$ respectively. If we obtain mean C_v from Giaque's work (*l.c.*) the ratios α/C_v are $2{\cdot}71 \times 10^{-6}$ and $2{\cdot}85 \times 10^{-6}$ respectively. The small difference is within the experimental errors of measurement. The Grüneisen formula (1) has also been verified by Aoyama and Ito in Japan (1939) in the range (0 to -196)° C. Their constants are the same as are given by Adenstedt.

Gold.—Nix and MacNair (*a*) found that their data (-187 to 730)° C. could be very accurately interpreted by the formula (1) if $\theta = 190$, $k = 3{\cdot}4$, and $Q_0 = 148{\cdot}8$ K. cals. The experimental values of C_v as obtained by

Clusius and Harteck (1928) do not differ very much from those given by $\theta = 190$, in the range studied by Nix and MacNair. Grüneisen (1926) has used the results of the earlier workers [Dorsey (1908) and Grüneisen (1910)], and explained their data by taking θ to be the same as used by Nix and MacNair. k and Q_0 are, however, slightly different, being 3·0 and 145 K. cals. respectively. Ebert (*l.c.*) whose data extend to 48° K. has used the same constants as Grüneisen. There is a small discrepancy of about 12% between the calculated and the experimental values at 48° K., but this is liable to disappear with the use of the experimental values of the specific heat.

Silver.—Nix and MacNair's data (*b*) in the range (− 186 to 25)° C. are explained very accurately by the equation (1) if $\theta = 215$, $k = 2{\cdot}42$ and $Q_0 = 109$ K cals. Their observations are in fair agreement with those of the earlier workers [Buffington and Latimer (1926), Dorsey (*l.c.*) and Ebert (*l.c.*)]. The latter's measurements go as low as 48° K. and his constants are $\theta = 223$, $k = 3{\cdot}2$ and $Q_0 = 112$ K. cals. The value of θ obtained from the specific heat data of Giaque is nearly 213° K. in the range in which the thermal expansion has been studied.

Lead.—Nix and MacNair (*b*) have used $\theta = 88°$ K., $Q_0 = 77{\cdot}84$ K. cals. and $k = 3{\cdot}19$ to explain their data (− 188 to − 25)° C. They are in fair agreement with the experimental work of the earlier workers [Ebert, *l.c.*, Grüneisen, *l.c.*, Dorsey (1908)]. Ebert's data extend to 48° K., and his constants are $\theta = 92{\cdot}0°$ K., $k = 3{\cdot}2$, and $Q_0 = 79{\cdot}6$ K; cals. According to Giaque's measurements (*l.c.*) of specific heat $\theta = 93°$ K. in the region studied for the thermal expansion.

3. *Body-Centred Metals*

Tungsten.—The measurements of Nix and MacNair (*b*) cover the range − 188 to 25° C. and were carried out on a sample of 99·95% purity. Their values of the mean coefficient for the range 0 to − 78° C. is identical with that of Disch (1921), who worked with a metal of doubtful purity. There is a small difference of 2 to 5% between their results for the mean coefficients and those of Hidnert and Sweeney (1925) who used a sample of 99·98% purity. Nix and MacNair have used formula (1) with the constants $\theta = 310°$ K. and $Q_0 = 471{\cdot}2$ K. cals. They have, however, used a surprisingly large value of 30·63 for k, which is fifteen times the value demanded by the Grüneisen theory (*l.c.*). The Grüneisen formula can, therefore, only be regarded as an interpolation formula. In Table I, we have given the value of the thermal expansion coefficient as calculated from the Grüneisen formula when $k = 2$, the value given by Grüneisen.

Other constants are the same as used by Nix and MacNair. The experimental values, shown in the table, are from the data of the same workers and have been calculated from the formula (1) by the use of their constants. This has been done, because the values so calculated fall exactly on the curves given by them. It can be seen that the difference between the theoretical and the experimental values increases systematically with the rise of temperature, the difference near the room temperature being of the order of 15%. Considering the great accuracy claimed by the experimenters, the difference must be interpreted as a definite breakdown of the Grüneisen theory.

TABLE I

Comparison of the Grüneisen theory with the experimental data for Tungsten

Temperature °K	$\alpha \times 10^6$ (Experimental)	$\alpha \times 10^6$ (Calculated) $k=2$
100	8·347	8·17
150	10·85	10·34
200	12·27	11·31
250	13·28	11·79
300	14·19	12·1

Lithium.—The thermal expansion coefficients of this metal were measured by Simon and Bergmann (*l.c.*), and the specific heats by Simon and Swain (1935). The ratio of the thermal expansion to the specific heat falls so rapidly with the decrease of temperature that no reasonable value of k in the equation (1) can fit the whole data. It is, therefore, generally recognized as a case of a definite breakdown of the Grüneisen theory. The ratio α/C_v has been given in Table II for illustrating the nature of the so-called anomaly. α have been taken from Lord's paper (1941), who has interpolated Simon and Bergmann's data for the purpose.

TABLE II

α/C_v for lithium

Temperature °K	C_v cals./deg. gm. mol.	$\alpha \times 10^6$	$\alpha/C_v \times 10^6$
100	3·02	18·5	6·13
120	3·59	24·5	6·81
140	4·01	29·6	7·38
160	4·34	33·7	7·76
180	4·57	37·0	8·10
200	4·78	39·7	8·31
220	4·94	41·9	8·48
240	5·09	43·6	8·57
280	5·31	46·2	8·70

Sodium.—The thermal expansion of sodium has been measured by Quimby and Seigel (1938) in the range (80–290)° K. In order to verify the Grüneisen theory, these authors have calculated the value of the ratio $\frac{l_T - l_{273}}{l_{273}(E_T - E_{273})}$, and shown it to be reasonably constant. Here l_T is the length at T° absolute and E is the thermal energy content already defined. The ratio, however, is reasonably constant, only because the change in length has been measured from 0° C. If we measure the changes of length over shorter intervals the ratio $\frac{l_{T_2} - l_{T_1}}{l_{273}[E_{T_2} - E_{T_1}]}$ does not remain constant and shows systematic deviations of the same type as are shown by the other body-centred metals tungsten and lithium. This can be seen from Table III, where we have used the experimental data of the above workers to calculate this ratio. The values of E have been taken from *Landolt and Bornstetns' Tables Zweit Erg.*, page 1238. It must be pointed out that with the use of the term $k\frac{E}{Q_0}$, the ratio will not change to the extent that it has been shown in Table III. A difference of about fifteen per cent. will, however, still remain in the values of the ratio at the highest and the lowest temperatures and is in all probability a real difference.

TABLE III

The ratio $\frac{l_{T_2} - l_{T_1}}{l_{273}[E_{T_2} - E_{T_1}]}$ *for sodium*

Temperature range ° K	$\frac{l_{T_2} - l_{T_1}}{l_{273}} \times 10^5$	$E_{T_2} - E_{T_1}$ cals./gm. mol.	$\frac{l_{T_2} - l_{T_1}}{l_{273}(E_{T_2} - E_{T_1})} \times 10^5$
80– 90	41	51	·804
90–100	43	53	·81
100–120	101	111	·91
120–140	110	115	·96
140–180	239	240	1·00
180–220	260	250	1·04
220–260	271	259	1·05
260–290	206	200	1·03

4. Silicon

The thermal expansion of metallic silicon was first measured by Valentiner and Wallot (1915) between 100 and 250° K. The ratio of the measured value of the coefficient of expansion to the specific heat determined by the later workers decreases very rapidly with the fall of temperature. At 100° K., they actually observed a negative coefficient of expansion. Simon

and Bergmann (*l.c.*) measured the thermal expansion of several specimens and found that each had a different thermal expansion. They came to the conclusion that the thermal expansion depends on the previous history of the specimen and that no conclusions as to the validity of the Grüneisen law can be drawn from it.

5. Discussion

It can be easily seen from this review, that the face-centred metals obey the Grüneisen formula (1) very satisfactorily above the liquid-air temperature. Below this temperature the data are scanty, but wherever they are available, the formula is fairly successful in interpreting the results of measurement. The small discrepancy noticed in one or two cases between the theoretical and the experimental values, is in all probability, due to the experimental errors. This leads us to the inevitable conclusion, that the Grüneisen constants of the different frequencies are so near each other that an average value works fairly successfully. In the case of the body-centred metals, and probably in the case of silicon also, the Grüneisen theory is not successful in interpreting the experimental data of thermal expansion. In this respect, the Grüneisen theory follows the well-known Debye theory of specific heats. It is well known that, with the single exception of gold, the specific heats of all the face-centred metals are correctly given by a Debye function upto fairly low temperatures. It is in the case of the body-centred metals and silicon that the theory meets with its difficulties. It was pointed out in the paper on the specific heat of metals (*l.c.*) that these difficulties have their origin in the fact, that one of the frequencies does not involve a change in the distance of the nearest neighbours and may, therefore, have a very small value. Saxena (1944), has shown that Nayar's observations (1944) on the variation of the Raman frequency of diamond with temperature, can be reconciled with its observed thermal expansion if two of the frequencies have a different Grüneisen constant from the rest. These frequencies happen to be those in which the C−C bond of the neighbouring atoms remains unaffected in length. In the present case also, the failure of the Grüneisen law seems to arise from the large differences existing between the Grüneisen constants of the various frequencies.

In conclusion, the author wishes to record his grateful thanks to Professor Sir C. V. Raman, KT., F.R.S., N.L., for his interest in the work.

Summary

The experimental data on the thermal expansion of the five face-centred metals, *viz.*, aluminium, silver, copper, gold and lead, of the three body-centred metals, namely, tungsten, lithium and sodium, and of silicon, have

been reviewed from the point of view of the Grüneisen theory. It has been found that the face-centred metals obey the Grüneisen law fairly satisfactorily, but the theory breaks down in the case of the body-centred metals. The experimental data on the thermal expansion of silicon are not sufficiently reliable for any conclusions to be drawn from it. It has been suggested that the failure of the Grüneisen law in the body-centred metals is intimately related with the breakdown of the Debye formula for the specific heat in the same metals, and arises from the fact that one of the frequencies of vibration does not involve any change in the distance of the nearest neighbours. This frequency may have a Grüneisen constant so different from the others that it may be difficult to find a suitable mean value for all the frequencies.

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THE MAGNETIC PROPERTIES OF TOURMALINE AND EPIDOTE

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Received September 1, 1944

(Communicated by Sir C. V. Raman, Kt., F.R.S., N.L.)

1. Introduction

As is well known, tourmaline is a complex silicate of aluminium and boron crystallising in the rhombohedral system. Its dichroism, and the piezo- and the pyro-electric properties exhibited by it make it a crystal of great interest to the physicist. A few observations of its magnetic behaviour are on record, the most recent being those by Wilson (1920) and by Grenet (1930). Numerous specimens of tourmaline of various shades of colour and transparency were available in the crystallographic collection of Sir C. V. Raman, and it appeared to be of interest to make a systematic investigation of their magnetic susceptibility and anisotropy. The specimens had their natural prismatic form, with a rounded triangular section, the sides being lustrous and marked with strong striations parallel to the axis, except No. 4 which was a plate cut perpendicular to the axis. The specimens were of different colours, black, brown, green, rose and white. Most of the specimens were transparent. No. 4 was transparent only at the edges which were thin, and No. 1 was completely opaque.

Epidote is an ortho-silicate of calcium, aluminium and iron, crystallising in the monoclinic system. The analysis of a number of specimens reported (Tempel, 1938) shows that iron is the chief paramagnetic element in it; the ferric oxide varies from 4% to 17%, and the ferrous oxide is usually much smaller, being less than 1% in the majority of the specimens. Two crystals of epidote were obtained from the crystallographic collection of Sir C. V. Raman, and their magnetic properties were studied. They were brownish-green in colour, and were bounded by well-developed crystallographic faces on all the sides, the crystals being in the form of short prisms, extending along the *b*-axis.

2. Experimental Results

For all the tourmalines, the susceptibility along the axis was less than that perpendicular to it, agreeing with Wilson's observation, and all the specimens were isotropic in the symmetry plane.

The magnetic susceptibility of the tourmalines perpendicular to the axis was measured by Rabi's null method. They were all paramagnetic, and a solution of manganous chloride was used for the bath. The displacement of the crystals in the bath was measured very sensitively by suspending it from the beam of a Curie-balance of low torsional constant, and observing the deflection of the beam with a lamp and scale, so that any field-dependence of the susceptibility of the specimens could be easily detected. For specimens Nos. 1 to 6, a small unbalanced deflection of the crystal in the bath was observed at low fields, showing that the susceptibility decreased very slightly with increase of field strength, presumably due to traces of ferromagnetic impurities. Since their deflection was negligibly small compared with the deflection produced in air, no correction was necessary for the effect of the ferromagnetic impurities. The fine rose-coloured specimens 6 to 11 were completely free from such impurities.

The anisotropy of the tourmalines was measured by Krishnan's torsional method. Since the crystals were appreciably asymmetric in shape, they were surrounded by the solutions of their own volume susceptibility while measuring the critical torsion. The difference between the susceptibilities perpendicular and parallel to the axis ($\chi_\perp - \chi_{11}$) was measured.

The results for the susceptibility and anisotropy, together with a description of the colour and density of the tourmalines are given in Table I.

TABLE I. *Tourmaline*

No.	Mass gm.	Specific Gravity	Colour	Mass Susceptibility $\chi \times 10^6$	Specific Anisotropy $(\chi_\perp - \chi_{11}) \times 10^6$
1	3·010	3·12	Black	13·4	2·01
2	0·554	3·15	Dark brown with a clear zone at one end	11·0	0·295
3	2·052	3·13	Uniform dark green	10·8	1·65
4	4·042	3·11	Black	10·1	0·577
5	3·514	3·10	Light green with a clear zone at one end	$9{\cdot}7_8$	0·226
6	1·402	3·08	Colourless with a small red spot	4·96	0·0584
7	3·102	3·03	Uniform rose	1·18	0·0379
8	3·305	3·04	Rose, one end denser in colour	$0{\cdot}96_9$	0·0121
9	5·787	3·05	Rose, half the length denser in colour	$0{\cdot}95_8$	0·0138
10	4·553	3·04	Uniform rose	$0{\cdot}73_9$	0·0168
11	1·953	3·03	Uniform light rose	0·583	0·0375

The two crystals of epidote were found to have $\chi_3 > \chi_2 > \chi_1$, where χ_3 is the susceptibility along the *b*-axis, and χ_1 and χ_2 are the susceptibilities along the maximum and minimum axes of magnetisation respectively in the *b*-plane. The magnetic anisotropies $\chi_1 - \chi_2$ and $\chi_3 - \chi_2$ were measured by finding the period of oscillation of the crystal in a uniform magnetic field when suspended with the χ_3 and χ_1 axes respectively vertical. The magnetic anisotropy was found to be small, being less than half a per cent. of the susceptibility.

The susceptibility of the epidotes along the χ_1 axis was measured by a Curie-balance, and was found to be practically independent of field-strength. The values $22{\cdot}7 \times 10^{-6}$ and $23{\cdot}6 \times 10^{-6}$ were obtained for the two specimens and the magnitude of the susceptibility indicates that the amount of ferric oxide required to give these values come within the range of values reported by Tempel. The results for epidote are given in Table II.

TABLE II. *Epidote*

No.	Mass gm.	Specific Gravity	Mass Susceptibility $\chi \times 10^6$	Specific Anisotropy $\Delta\chi \times 10^6$
1	2·617	3·46	22·7	$\chi_1 - \chi_2 = 0{\cdot}094$ $\chi_1 - \chi_3 = 0{\cdot}046$
2	0·855	3·45	23·6	$\chi_1 - \chi_2 = 0{\cdot}077$ $\chi_1 - \chi_3 = 0{\cdot}066$

It will be seen from Table I that the brown, green and black tourmalines have a higher susceptibility and higher anisotropy, and also exhibit a greater density, associated presumably with a greater content of paramagnetic iron or chromium ions. The rose-coloured tourmalines have a low magnetic susceptibility and anisotropy, and also a slightly lower density. It may be remarked also that the characteristic variation of the intensity of the light transmitted by the tourmaline with the direction of the electric vector was generally more conspicuous for the tourmalines of the former kind which exhibit a high magnetic anisotropy.

In conclusion, the author wishes to record his deep sense of gratitude to Professor Sir C. V. Raman for suggesting the problem, for the loan of the crystals, and for the keen interest he took in the progress of the work.

3. *Summary*

The magnetic susceptibility and anisotropy, and also the density, of 11 specimens of tourmalines of different shades of colour and of 2 specimens of

epidote have been measured and are reported. The susceptibility of the tourmalines varied from 13·4 to 0·58 $\times 10^{-6}$, and the anisotropy from 2·1 to 0·01 $\times 10^{-6}$. It was found that those specimens which had a higher susceptibility had, in general, a larger anisotropy and a higher density. Their colour was also dark brown or black. Their dichroism was also more pronounced than with the rose-coloured specimens possessing low susceptibility. The mass susceptibility of the two specimens of epidote were 22·7 and 23·6 $\times 10^{-6}$. Their anisotropy was found to be extremely small, being less than 0·5% of the susceptibility.

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MAGNETIC BEHAVIOUR OF IRON-PYRITES

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Received September 1, 1944

(Communicated by Sir C. V. Raman, Kt., F.R.S., N.L.)

1. Introduction

Iron-Pyrites (FeS_2) is a mineral crystallising in the cubic system and its magnetic properties are of considerable interest. A survey of the literature regarding its magnetic susceptibility shows that there are very wide variations in the results obtained by the different workers, values ranging from $0{\cdot}9 \times 10^{-6}$ to 159×10^{-6} being quoted by J. W. Mellor. Jackson (1929) has observed that its susceptibility is independent of temperature and several workers have described it as "non-magnetic".

The specimens of pyrites used for study were taken from the crystallographic collection of Sir C. V. Raman, having been originally received by him from the Director of the Nepal Bureau of Mines, Khatmandu. For the most part they were brilliant crystals with a bright metallic lustre and were in the form of cubes with their faces well developed and of a tin-white colour (and not brass yellow as is usually described). From a large stock of these specimens, forty-four crystals were chosen for study with masses varying between 2·2 gm. and 0·35 gm. One sample which had undergone alteration to limonite and had a dark brown colour was also studied.

In view of the fact that the crystals were tin-white in colour and not brass yellow, a chemical analysis was carried out on a portion of crystal No. 37 which had a bright metallic luster. A qualitative analysis did not reveal the presence of Cu, Co, Ni, As, Sb or Bi in it. A sample of the specimen heated in a current of air evolved sulphur-dioxide which was evident by its smell and its decolourising action or an acidulated solution of potassium permanganate. A quantitative estimate of the iron present in it showed that it contained 47·8% of Fe (the % of Fe according to the formula FeS_2 being 46·5).

The specific gravity of six of the crystals (Nos. 33, 35, 36, 37, 40 and 42) was also determined and a uniform value of 5·02 was obtained; which is in the range of the specific gravity reported for iron-pyrites.

2. *Variation of the Susceptibility with the Specimen*

An approximate determination of the susceptibility of thirty of the specimens (Nos. 1 to 30) was made by observing the deflection they produced in the Curie-balance. The value of the mass susceptibility ranged from $0{\cdot}2 \times 10^{-6}$ to about 190×10^{-6}, thirteen crystals having values between $0{\cdot}2 \times 10^{-6}$ and $0{\cdot}25 \times 10^{-6}$, five between $0{\cdot}3 \times 10^{-6}$ and $0{\cdot}35 \times 10^{-6}$, six between $0{\cdot}4 \times 10^{-6}$ and $0{\cdot}45 \times 10^{-6}$, and one specimen No. 30 had the large value of 190×10^{-6}.

An accurate determination of the susceptibility of the remaining fifteen specimens (No. 31 to 45) was made. Crystals 31 to 43 whose susceptibility was low were measured by the Rabi's null method, using a dilute solution of $MnCl_2$ for the bath. The crystal was suspended in a non-homogeneous field from the beam of a Curie-balance, the deflection of which was observed by a lamp and scale. A thin wire was used for the suspension so that large deflections were produced by the crystals in air. For all the crystals when the volume susceptibility of the solution was approximately equal to that of the crystal, the deflection of the balance at low fields showed that the crystal was paramagnetic with respect to the solution and this deflection diminished as the field strength increased, showing thereby that the susceptibility decreased slightly as the field strength increased. This disturbance of the balance point at low fields was exceptionally large for crystal No. 43. The crystals (except No. 43) were saturated magnetically for currents above about 7 amp. and in all cases the bath was adjusted to give exact balance for a current of 12·5 amp.

Crystal No. 44 which had its surface altered into limonite and No. 45 had large susceptibility and were measured by the Curie-balance with a thicker suspension, by comparison with a strong solution of manganous chloride. Crystal No. 44 had a field independent susceptibility and No. 45 showed large variations with field strength. The results obtained for the fifteen specimens at the room temperature (25° C. to 27° C.) are tabulated below,

TABLE I

Mass Susceptibility χ *of crystals* 31 *to* 45

Crystal No.	31	32	33	34	35	36	37	38
$\chi \times 10^6$	0·202	0·208	0·220	0·222	0·223	0·252	0·256	0·289
Crystal No.	39	40	41	42	43	44	45	
$\chi \times 10^6$	0·326	0·329	0·377	0·477	3·3	13·0	24·0	

the values for crystals 31 to 43 being for a field strength of 8,400 oers and for crystals 44 and 45 for a field strength of 4,800 oers.

3. *Variation of Susceptibility with Field Strength*

From the above studies it was clear that the susceptibility of the crystals varied with field strength and this variation was further investigated for two crystals, one having a low susceptibility and the other having a high susceptibility. Crystals No. 37 and No. 45 were chosen for this purpose; the former, a portion of which had been previously analysed was a cleavage piece of mass 0·728 gm. with susceptibility $0{\cdot}256 \times 10^{-6}$ at a field strength of 8,400 oers, and the latter was in the form of a cube of mass 0·520 gm. with susceptibility $24{\cdot}0 \times 10^{-6}$ at a field of 4,800 oers. The values are given in Table II for crystal No. 37 and in the first column of Table IV for crystal No. 45.

TABLE II

Variation of χ of Crystal No. 37 with Field Strength

Field strength (oers.)	3000	3500	4000	4400	4800	8400
$\chi \times 10^6$	0·277	0·264	0·258	0·257	0·257	0·256

4. *Variation of the Susceptibility with Temperature*

The dependence of the susceptibility on temperature was investigated using the Curie-balance for the crystals No. 37 and No. 45 which were chosen as typical of the low and the high susceptibility specimens respectively. An electric heater was used and the pole-pieces of the magnet were

TABLE III

Variation of χ of Crystal 37 with Temperature

Temperature °C.	$\chi \times 10^6$
26	0·257
54	0·252
98	0·247
150	0·246
204	0·242
247	0·241
304	0·240
After cooling to 26° C.	0·263

N.B.—A change of the colour of the surface to pale yellow was observed after the crystal had cooled to room temperature.

TABLE IV

Variation of χ of Crystal No. 45 with Temperature and with Field Strength

Field strength (oers)	$\chi \times 10^6$			
	25° C.	52° C.	102° C.	After cooling to 26° C.
3000	37·3	..	36·4	37·6
3500	32·3	31·7	31·5	32·6
4000	28·8	28·9	28·4	29·2
4400	25·8	25·8	25·3	26·2
4800	24·0	23·9	23·6	24·2

protected from the heater by surrounding them with water jackets. Crystal No. 37 was studied up to 304° C. from the room temperature at a field of 4,800 oers; and since it had a low susceptibility account was taken of the change of the susceptibility of the surrounding air with temperature. Crystal No. 45 was studied up to 102° C. at fields ranging from 3000 oers to 4800 oers. The results are given in Tables III and IV.

5. *Magnetic Anisotropy of the Specimens*

The possible variation of the susceptibility with direction was tested for all the specimens by suspending them in a uniform magnetic field by a fine quartz fibre and observing their tendency for orientation. The crystal Nos. 30, 43 and 45 took up definite orientation in the field while the rest of the specimens were found to be isotropic.

For investigating the variation of the susceptibility with direction in the highly ferromagnetic crystal No. 45 it was suspended in the magnetic field with one of the cube-faces horizontal; and with the help of a light aluminium disc graduated in degrees and a light pointer attached to the suspension, the crystal was fixed at angular intervals of 15° and the deflection of the Curie-balance observed. Two directions perpendicular to each other were noted, one for which the pull was maximum (12·4 cm.) and the other for which it was minimum (11·8 cm.) thus showing a difference of about 5% between the susceptibilities in the two directions.

6. *Remanent Magnetism*

Crystal No. 45 was tested for remanent magnetisation. It was thoroughly demagnetised, suspended by a fine quartz fibre and its period of oscillation in the earth's magnetic field determined. It was then magnetised in the strong field of an electromagnet and again its period of oscillation

in the earth's field was determined. In both cases the period was found to be 5·83 sec. showing that there was practically no remanent magnetisation.

7. *Discussion*

The mass susceptibility of the crystals vary within the wide range $0{\cdot}2 \times 10^{-6}$ to 190×10^{-6} and the distribution of the specimens within this range is very striking. The results indicate that the susceptibility tends to a lower limit of about $0{\cdot}2 \times 10^{-6}$ and the majority of the specimens lie near this lower limit. The susceptibility rapidly increases to very high values and the number of specimens possessing high values is very small; only three crystals Nos. 30, 43 and 45 were obtained falling within the range $3{\cdot}3 \times 10^{-6}$ to 190×10^{-6} out of a total of forty five crystals examined. Crystal No. 44 which had its surface altered into limonite had a high susceptibility of $13{\cdot}0 \times 10^{-6}$ which was independent of field strength and this high susceptibility is attributable to the chemical change that had taken place in it. The variation of the susceptibility observed in the other specimens is of considerable interest especially in view of the fact that the crystals appeared identical in respect of properties such as colour, lustre, form, etc. The crystals Nos. 30, 43 and 45 were distinguished from the others only by their magnetic anisotropy and high susceptibility. Since the crystals were all without any observable imperfections and had a bright metallic surface, it is difficult to believe that the differences of susceptibility from specimen to specimen arise from impurities or from differences of chemical composition of the mineral. It seems not improbable that these remarkable variations in the magnetic behaviour of iron-pyrites are a characteristic property of this crystal.

It is a remarkable fact also that for all the specimens measured accurately the susceptibility varied with the field strength. The qualitative observations made on the disturbance of the balance-point of the crystal in the bath, at low fields, showed that the field-dependence of the susceptibility was greater for specimens of higher susceptibility. For specimen No. 43 which had a high susceptibility, this dependence was observed to be very large. The detailed measurements of the variation of the susceptibility with field strength on crystals No. 37 and No. 45 clearly bring out this fact. Thus the field-dependence of the susceptibility increasing with the value of the susceptibility also seems to be a definite characteristic of iron-pyrites.

The magnetic susceptibility of the crystals is practically independent of temperature. A very small decrease of susceptibility is observed as the temperature increases for the two crystals studied; this is much smaller than what is observed in the case of the normal paramagnetics. For crystal

No. 37 the fractional decrease amounts to about 1/4000 per degree and for crystal No. 45 also it is of the same order.

The author's sincere gratitude is due to Professor Sir C. V. Raman for suggesting the problem, for the loan of the crystals and for his keen interest and guidance during the progress of this work. The author's thanks are also due to the Director of Nepal Bureau of Mines, Khatmandu, from whom the crystals were obtained.

8. *Summary*

Magnetic studies were made on forty-five specimens of iron-pyrites from Nepal. They were tin-white in colour and had a bright metallic lustre, except one specimen which was dark brown owing to alteration into limonite. One of the specimens with the bright surface was analysed and found to contain 47·8% of Fe. The specific gravity of six of these gave the value of 5·02. The susceptibility varied in the large range from about $0{\cdot}2 \times 10^{-6}$ to about 190×10^{-6}; most of the specimens had values near the lower limit and only a few had high values. The susceptibility of all the specimens showed a decrease with increase of field strength; the dependence on field strength was small for the low-susceptibility specimens and it was greater for those having higher susceptibility. The specimen which was altered into limonite had a high but a field-independent susceptibility. The susceptibilities of the two crystals, one having a low susceptibility and the other having a high susceptibility, were nearly independent of temperature; only a very small decrease was observed with increase of temperature. All the crystals having low susceptibility were magnetically isotropic and the three crystals which had high susceptibility were anisotropic; and one specimen of the latter group was tested and found to have no remanent magnetisation.

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